Kinetic analysis of thermite reaction in Al–Ti–Fe₂O₃ system to produce (Fe,Ti)₃Al–Al₂O₃ nanocomposite

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In this study, (Fe,Ti)₃Al–Al₂O₃ nanocomposite was synthesized by mechanical alloying (MA) of Al–Ti–Fe₂O₃ powder mixture. Structural evolution and thermal analysis of powder particles during MA were studied by X-ray diffractometry (XRD) and differential thermal analysis (DTA). Kinetic analysis of Fe₂O₃–Al reaction was conducted using free model methods. The (Fe,Ti)₃Al–Al₂O₃ nanocomposite was formed during MA via Fe₂O₃–Al thermite reaction. The Fe₂O₃–Al reaction appeared to occur in combustion mode and the formation of (Fe,Ti)₃Al–Al₂O₃ nanocomposite occurred in two consecutive stages. In the first stage, Al₂O₃ and in the second stage, (Fe,Ti)₃Al phases were formed. Kinetic analysis revealed that for ball milled powders the reaction of Fe₂O₃ with Al can take place below Al melting temperature with a different reaction path.

1. Introduction

Fe₃Al based intermetallics have attractive properties like high hardness, high melting point and excellent oxidation and corrosion resistance [1] making them useful for several structural applications including gas metal filters, heating element, heat treatment fixtures, high temperature dies and molds and cutting tools [2,3]. Addition of a third alloying element such as Ti, Cr, … to Fe₃Al intermetallic compound can improve mechanical properties in particular ductility at room temperature by mechanisms such as solid solution and/or precipitation hardening as well as grain boundary modification [4–6]. It has also been shown that the dispersion of hard second phase particles (e.g., Al₂O₃) in the matrix can enhance the mechanical properties [7]. Intermetallic based composites reinforced by alumina exhibit high strength, good wear resistance and improved fracture toughness [8,9]. In situ formation of Al₂O₃ in Fe₃Al matrix can be readily achieved by ball milling of Fe₂O₃ with Al powder mixture via the solid-state displacement reaction of 2Al + Fe₂O₃ = 2Fe + Al₂O₃. There are several methods for estimating kinetic parameters of solid-state reactions based on differential thermal analysis (DTA) and differential scanning calorimeter (DSC) data. Among these free model methods, the Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), Tang and Starink are the most reliable methods for calculating activation energy of thermally activated reactions [10]. Patankar and Fores [11] studied the formation of Nb₅Sn compound by MA of Nb and Sn elemental powders. They reported that after 3 h MA a Nb(Sn), solid solution is formed. Through Kissinger–Akahira–Sunose and Flynn–Wall–Ozawa methods, the activation energy was calculated to be about 312 kJ·mol⁻¹. Fan et al. [12] studied the kinetics of thermite reaction in 8Al–3Fe₂O₃ system. Their results showed that thermite reaction during DSC run occurred after melting of Al. Also, an activation energy of 145 kJ·mol⁻¹ was reported for thermite reaction in this system, indicating that the diffusion of Al in FeAl₂O₄ compound controls the thermite reaction. Mostaan et al. [13] studied the kinetics of formation of Al₂O₃/Nb composite by four isocoonversional methods (KAS, FWO, Tang and Starink). Their results showed that all methods lead to a similar value of activation energy. In our previous work, the (Fe,Ti)₃Al–Al₂O₃ nanocomposite was synthesized by mechanical alloying (MA) starting from Fe–Al and TiO₂ powder mixture [14]. In the present work (Fe,Ti)₃Al–Al₂O₃ nanocomposite was synthesized by MA of Al–Ti and Fe₂O₃ powder mixture. The kinetics of thermite reaction were studied to gain further insight into the formation mechanism of (Fe,Ti)₃Al–Al₂O₃ nanocomposite by MA route.

2. Experimental methods

Fe, Al, Ti and Fe₂O₃ powders with a purity higher than 99% were used as starting materials. Al particles were irregular in shape with size distribution of about 50–100 μm. Ti particles had an irregular shape with porous structure and size distribution of about 400–500 μm. Fe₂O₃ powder had irregular particles with size distribution of about 0.5–4 μm. Al, Ti and Fe₂O₃ powders were mixed according to reaction [4]. MA was carried out in a high energy planetary ball mill, nominally at room temperature and under Ar atmosphere. The details of MA conditions are reported elsewhere [15]. Samples were taken at selected time intervals and characterized by X-ray diffraction (XRD) in a Philips X’PERT MPD diffractometer using filtered Cu Kα radiation (λ = 0.1542 nm). Annealing of powder particles was carried out to study the thermal
behavior of milled powders. A small amount of powder was sealed and annealed up to 900 and 1200 °C in a conventional furnace with a heating rate of 5 °C/min and then cooled in air. The structural transitions occurring during annealing were determined by XRD. The crystallite size and internal strain of powders were estimated using the Williamson–Hall method [16]. The kinetic parameters were obtained by DTA in Perkin-Elmer DSC-7 analyzer, in 25–1200 °C temperature range, under Ar atmosphere and in three different heating rates of 5, 15 and 20 °C/min. The baseline for DTA traces was calculated by software provided in the Perkin-Elmer DSC-7 analyzer.

3. Results and discussion

3.1. Thermodynamic aspects of Fe₂O₃–Al reaction

Reaction of Fe₂O₃ with Al producing Fe and Al₂O₃ phases is as follows:

\[
2\text{Al} + \text{Fe}_2\text{O}_3 = 2\text{Fe} + \text{Al}_2\text{O}_3
\]

\[
\Delta H_{298}^0 = -840 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
\Delta G_{298}^0 = -852 \text{ kJ} \cdot \text{mol}^{-1}
\]

The reaction (1) is extremely exothermic (\(\Delta H_{298}^0 \ll 0\)) and can thermodynamically occur at ambient temperature as its \(\Delta G_{298}^0\) is negative.

\[
\Delta H_{298}^0 = \sum \Delta H_{298}^0 (\text{Product}) - \sum \Delta H_{298}^0 (\text{Reactant}) \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
\Delta G_{298}^0 = \Delta H_{298}^0 - T \Delta S_{298} \text{ kJ} \cdot \text{mol}^{-1}
\]

Adiabatic temperature, \(T_{\text{ad}}\), for this reaction was calculated to be about 2690 °C. As a result, reaction (1) occurs in combustion mode during MA. In the current study, extra Al (1 mol) and Ti (1 mol) powders were added to the powder mixture to produce (Fe,Ti)$_3$Al matrix. The excess Al and Ti elements act as diluting agents and reduce \(T_{\text{ad}}\) to 2152 °C, indicating that reaction (1) could occur in combustion mode during MA even in the presence of diluents.

3.2. Structural evolution

(Fe,Ti)$_3$Al–45 vol.% Al$_2$O$_3$ nanocomposite was synthesized according to the following reaction:

\[
3\text{Al} + \text{Ti} + \text{Fe}_2\text{O}_3 = (\text{Fe},\text{Ti})_3\text{Al} + \text{Al}_2\text{O}_3.
\]

Fig. 1 shows the XRD patterns of 3Al–Ti–Fe₂O₃ powder mixture as-received and after different milling times. As can be seen, in as-received powder, only Al, Ti and Fe₂O₃ peaks are seen. By increasing milling time to 2 h, the intensity of Al, Ti and Fe₂O₃ diffraction peaks decreased and their width increased due to the internal strain induced by lattice defects and refinement of crystallite size.

The XRD pattern of the 5 h milled sample revealed that Al reacted with Fe₂O₃ forming (Fe,Ti)$_3$Al and Al₂O₃ phases. Further milling led to the broadening and decreasing of (Fe,Ti)$_3$Al and Al₂O₃ peaks. Crystallite size and internal strain of (Fe,Ti)$_3$Al and Al₂O₃ phases after 100 h of MA were calculated to be about 10 ± 3 nm, 0.95 ± 0.1%, 20 ± 5 nm and 3 ± 0.2%, respectively. Therefore, XRD results accord well with the thermodynamic prediction and confirm that the reaction of Al with Fe₂O₃ occurs in a manner similar to self-propagating high temperature synthesis (SHS) mode. It has been reported that in Fe–Al–TiO₂ system, the (Fe,Ti)$_3$Al intermetallic compound is completely formed after 40 h of MA, while in Al–Ti–Fe₂O₃ system, the intermetallic compound was rapidly formed after 5 h of MA [14]. This is because in Al–Ti–Fe₂O₃ powder mixture, the reaction between Al and Fe₂O₃ occurred in combustion mode and the heat released by this reaction accelerated (Fe,Ti)$_3$Al formation. This implies that reaction (4) during MA includes two consecutive stages according to the following reactions:

\[
2\text{Al} + \text{Fe}_2\text{O}_3 = 2\text{Fe} + \text{Al}_2\text{O}_3
\]

\[
2\text{Fe} + \text{Al} + \text{Ti} = (\text{Fe},\text{Ti})_3\text{Al}.
\]

3.3. Thermal analysis of powders

DTA of powder particles was conducted to determine the effect of milling on kinetics of Fe₂O₃–Al reaction. For this purpose, powders milled for 2 and 4 h (before thermite reaction) were selected. As seen

![Fig. 1. XRD patterns of 3Al–Ti–Fe₂O₃ powder mixture at different milling times.](image-url)
in Fig. 2 the XRD pattern of the sample milled for 4 h includes only the peaks of initial powder mixture. Results of DTA for samples milled for 2 and 4 h are presented in Fig. 3.

The sample milled for 2 h showed two exothermic peaks at 870 and 1110 °C and one endothermic peak at 659 °C. The endothermic peak was related to Al melting. In order to determine the nature of exothermic peaks, samples heated to 900 and 1200 °C were analyzed by XRD. The results are presented in Fig. 4. As can be seen, after heating up to 900 °C, Al2O3, Fe, Ti and Al peaks are presented in the XRD pattern, indicating that the first exothermic peak on the DTA curve is related to the reaction between Al and Fe2O3 (reaction (5)). Fig. 4b indicates the XRD patterns after heating up to 1200 °C. As it is clear, only (Fe,Ti)3Al and Al2O3 peaks exist on the XRD pattern, indicating that the second exothermic peak on the DTA curve is related to the formation of (Fe, Ti)3Al intermetallic compound according to reaction (6). These results confirm that reaction (4) occurs in two consecutive stages during heating. Comparison of DTA curves of two samples (Fig. 3) indicates that in the sample milled for a longer time (4 h), Fe2O3–Al reaction takes place before Al melting and two exothermic peaks become closer. This indicates that with increasing milling time, the formation of (Fe,Ti)3Al–Al2O3 structure appears to take place as a single stage on XRD.

3.4. Kinetic analysis

Transformation rate of a given solid-state reaction in isothermal conditions is related to the temperature \((T)\) and degree of conversion \((\alpha)\) according to the following relationship:

\[
\frac{d\alpha}{dt} = \frac{k(T)f(\alpha)}{\beta}
\]  

where \(k(t)\) is the reaction rate constant, \(f(\alpha)\) is the reaction model, and \(\alpha\) is the extent of transformation. Under non-isothermal conditions, with constant heating rate of \(\beta = \frac{dT}{dt}\), the kinetic relation can be expressed by the following equation:

\[
\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha)
\]  

where \(A\) is the pre-exponential factor \((s^{-1})\), \(E\) is the activation energy \((kJ\cdot mol^{-1})\), and \(R\) is the universal gas constant. This equation can be integrated by the separation of variables:

\[
\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^t \exp\left(-\frac{E}{RT}\right) \frac{dT}{\frac{dT}{dt}} = \frac{AE}{\beta R} \int_0^t \exp\left(-\frac{E}{RT}\right)dY.
\]  

where \(\alpha\) is the extent of transformation. The right-hand integral, usually called temperature integral, \(P(Y)\), does not have any analytical solution.

\[
P(Y) = \frac{A}{\beta} \int_0^Y \exp\left(-\frac{E}{RT}\right) dY.
\]  

Temperature integral can be solved using several approximations which lead to the isoconversion method, as expressed below:

\[
\ln\left(\frac{\beta}{T}\right) = C - \frac{E}{RT}
\]  

Different methods have been introduced for calculating activation energy. Among them, the most popular ones are:

1. Kissinger–Akahira–Sunose (KAS) method [18–20], that is expressed as follows:

\[
\ln\left(\frac{\beta_i}{T_i^2}\right) = C_k(\alpha) - \frac{E\alpha}{RT_i}
\]

where the \(C_k(\alpha)\) is calculated by:

\[
C_k(\alpha) = \ln\left(\frac{AR}{E\alpha}\right).
\]

2. Flynn–Wall–Ozawa (FWO) method, which was independently suggested by Flynn and Wall [21] and Ozawa [22]:

\[
\ln(\beta_i) = C_w(\alpha) - 1.0518 \frac{E\alpha}{RT_i}
\]
3. Tang method [23], that is given by:

$$\ln \left( \frac{\beta_i}{T_{\text{calc}}} \right) = C_i(\alpha) - 1.0014 \frac{E_c}{R T_{\text{calc}}}.$$  \hspace{1cm} (15)

4. Starink method [24,25], which is expressed as follows:

$$\ln \left( \frac{\beta_i}{T_{\text{calc}}} \right) = C_i(\alpha) - 1.0008 \frac{E_c}{R T_{\text{calc}}}.$$  \hspace{1cm} (16)

3.4.1. Kinetic studies of Fe₂O₃ reduction by Al in Al–Ti–Fe₂O₃ system

As previously mentioned, the reaction of Fe₂O₃ with Al in Al–Ti–Fe₂O₃ system during MA occurred after 4.5 h. Therefore, samples milled for 2 and 4 h were highly activated. Fig. 5 shows DTA curves of the sample milled for 2 h heated with different rates. As can be seen, by increasing the heating rate up to 15 °C/min, the first exothermic peak displaced to the higher temperatures, whereas the second exothermic peak disappeared. It is due to the displacement of the second peak to temperatures higher than 1200 °C. By increasing the heating rate up to 20 °C/min, the first exothermic peak, which was related to Fe₂O₃–Al reaction, was displaced to 1040 °C. Also, with increasing heating rate, the peak height was increased.

![DTA curves of (a) 2 h milled sample and (b) 4 h milled sample.](image)

![XRD patterns of 3Al–Ti–Fe₂O₃ powder mixture (a) after 2 h MA and subsequent heating up to 900 °C with the heating rate of 5 °C/min and (b) after 2 h MA and heating up to 1200 °C with the heating rate of 5 °C/min.](image)
The activation energy of Fe₂O₃–Al reaction for the sample milled for 2 h at \( \alpha = 0.5 \) (apparent activation energy) was calculated by different methods given in Section 3.4. The curves plotted for calculating the apparent activation energy \( (E_a) \) are presented in Fig. 6. The results are presented in Table 1. The values of apparent activation energy obtained by four methods are similar. Fan et al. [12] studied the kinetics of Fe₂O₃–Al reaction after 30 min MA using the Starink method. They reported that the activation energy was about 145 kJ·mol⁻¹. However, in the present study, the apparent activation energy for Fe₂O₃–Al reaction was measured to be about 83.1 kJ·mol⁻¹ using the same method. This difference in \( E_a \) values is probably due to the longer milling times and the presence of Ti in the powder mixture.

Fig. 7 shows the activation energy \( (E_a) \) versus the degree of transformation \( (\alpha) \) calculated by the Kissinger method. As can be seen, \( E_a \) is independent of \( \alpha \) suggesting that the mechanism of reaction remains unchanged with time. This shows that reaction kinetics is controlled by a single-step mechanism. Generally, the change in \( E_a \) with \( \alpha \) occurs for reactions with multi-step mechanism [26].

![Fig. 5. DTA curves of 3Al–Ti–Fe₂O₃ powder mixture after 2 h MA at different heating rates.](image)

**Table 1**
The calculated apparent activation energy by different methods for thermite reaction.

<table>
<thead>
<tr>
<th>Method</th>
<th>Kissinger–Akahira–Sunose</th>
<th>Flynn–Wall–Ozawa</th>
<th>Tang</th>
<th>Starink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent activation energy (kJ·mol⁻¹)</td>
<td>82.3 ± 4%</td>
<td>97 ± 3%</td>
<td>83.3 ± 3%</td>
<td>83.1 ± 4%</td>
</tr>
</tbody>
</table>
In some cases, the change in the reaction mechanism changes the pre-exponential factor rather than the activation energy [27]. The results showed that the pre-exponential factor is almost constant ($2.1 \times 10^5 - 4.9 \times 10^5$ s$^{-1}$).

The change of $\alpha$ as a function of temperature for Fe$_2$O$_3$–Al reaction is presented in Fig. 8. As can be seen, $\alpha$–$T$ curves for all three heating rates have an S shape indicating that with increasing heating rate, the reaction mechanism is constant and the free model methods can be applied.

Fig. 7. The activation energy changes for thermite reaction versus the degree of conversion.

Fig. 8. Degree of conversion versus temperature for Fe$_2$O$_3$–Al reaction at different heating rates.

Fig. 9. DTA curves of 3Al–Ti–Fe$_2$O$_3$ powder mixture after 4 h MA at different heating rates.
2. The (Fe,Ti)3Al reaction occurred in solid-state without Al melting. These results indicate that increasing milling time decreases the activation energy. In fact, as pointed out, for the sample milled for 4 h was calculated by the Kissinger method for the activation energy of Fe2O3. The Kissinger method was used to calculate the apparent activation energy. The Kissinger method is based on the following equation:

\[ \ln(\beta/T^2) = \frac{E_a}{R} - \frac{E_a}{RT} \]

where \( E_a \) is the apparent activation energy, \( R \) is the gas constant, \( \beta \) is the heating rate, and \( T \) is the temperature.

4. Conclusions

(Fe,Ti)3Al–Al2O3 nanocomposite powder was successfully synthesized by MA of the Al–Ti–Fe2O3 powder mixture. Kinetics of Fe2O3–Al reaction in this system was analyzed by free model methods and the following results were obtained:

1. MA of Al–Ti–Fe2O3 powder mixture led to in-situ formation of (Fe, Ti)3Al–Al2O3 nanocomposite via the reaction of Fe2O3 with Al. This reaction occurred in combustion mode and ordered (Fe,Ti)3Al intermetallic compound and crystalline Al2O3 phase were formed. By increasing milling time up to 100 h, the ordered DO3 structure was transformed to the disordered structure.

2. The (Fe,Ti)3Al–Al2O3 nanocomposite formed in two steps. In the first stage, the reaction of Fe2O3 with Al produces Fe and Al2O3 phases. This is followed with alloying of Fe, Ti and the remaining Al to form (Fe,Ti)3Al phase.

3. Increasing the milling time from 2 to 4 h reduced the onset temperature of Fe2O3–Al reaction to a temperature below Al melting temperature.

4. Changing the reaction path and mechanism in Al–Ti–Fe2O3 system with milling time increases the activation energy of Fe2O3–Al reaction.

References